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THIN-FILM INSULATORS AND METHOD FOR THEIR MANUFACTURE

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THIN-FILM INSULATORS AND METHODS FOR THEIR MANUFACTURE
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Claims

1. Thin-film insulators made of essentially amorphous silicon nitride, characterized in that the atomic percentage of silicon in the insulators is 40%-90% and the atomic percentage of nitrogen is 10%-60% (however, the aforementioned percentage is based on the total number of silicon atoms and nitrogen atoms in the insulators).

2. A method for manufacturing thin-film insulators, characterized by including the process of forming an essentially amorphous silicon nitride film on a substrate by ion-beam sputtering

deposition using a mixture of inert gas and nitrogen gas or inert gas and nitrogen atom-containing gas such as ammonia.

3. A methods for manufacturing thin-film insulators, characterized by including the process of depositing an essentially amorphous silicon nitride film on a substrate by ion-beam sputtering deposition using an inert gas and at the same time forming an essentially amorphous silicon nitride film on the substrate by irradiating the substrate with a charged particle beam made of nitrogen ions or ions of nitrogen atom-containing gaseous compounds such as ammonia gas.

Detailed description of the invention

The present invention pertains to silicon nitride and its manufacturing methods. More specifically it pertains especially to amorphous silicon nitride insulating films and their manufacturing methods which (the amorphous silicon nitride insulating films) are suitable to be used as insulators which constitute semiconductor devices and their integrated circuits or Josephson elements and their integrated circuits.

Heretofore, thin-film silicon nitride has been used in the fabrication of semiconductor devices, that is, as diffusion masks or insulating films of MIS elements. And thermal nitridation, the CVD method, or the plasma sputtering method was used for manufacturing such thin-film silicon nitride. However, the temperature for manufacturing silicon nitride thin films is approximately 1000°C or greater when the thermal nitridation method is used and is approximately 700°C or greater when the CVD method is used, which are very high temperatures, therefore it was impossible to form (or deposit) a silicon nitride thin film on a substrate which was not resistant to heat, which was a drawback. On the other hand, when the plasma CVD method and plasma sputtering method are used, silicon nitride thin films can be manufactured even when the manufacturing temperature is maintained at room temperature, therefore it is impossible to form (or deposit) a silicon nitride thin film on a substrate which is not resistant to heat. Therefore the method can be used, for example, in formation of passivation films of LSI. However, the quality of the silicon nitride films manufactured using said method differs very much depending on the film formation (or deposition) conditions thus it is difficult to optimize the conditions and moreover there is a difficulty in controlling the compactness of the films, for example, in films which are as thin as approximately 10 nm or less, the electric insulating properties of the films drop due to the presence of pinholes, which is a drawback.

The object of the present invention is to eliminate these drawbacks and to deposit compact silicon nitride insulating films with good electric insulating properties on substrates which are not resistant to heat.

To attain such objects, in the present invention an essentially amorphous silicon nitride film is formed (or deposited) on a substrate by sputtering deposition on the substrate with an ion

beam using an inert gas and simultaneously the substrate is irradiated with nitrogen ions or ions of nitrogen atom-containing gas. In the following, the present invention will be explained in detail using application examples.

Application Example 1

Figure 1 illustrates the amorphous silicon nitride manufacturing apparatus used in Application Example 1. In the Figure 1, 1 is a vacuum vessel, 2 is a vacuum pump, 3 is an ion beam generator, 4 is a gas introduction tube, 5 is a gas flow rate adjusting apparatus, 6 is a gas cylinder, 7 is a target, and 8 is a substrate.

In the present application example the gas in the gas cylinder 6 is a mixture of argon gas and nitrogen gas or a mixture of argon gas and nitrogen atom-containing gas such as ammonia gas, however, other inert gases such as xenon or krypton, etc. may be used instead of argon gas. The target is a silicon plate which is 99.999% pure, however, a silicon nitride (Si_3N_4) plate may be used instead. Substrate 8 is a thermally oxidized silicon wafer substrate, however, other insulator substrates such as glass plate, metal plate, semiconductor substrate, or organic polymer substrate may be used also.

Next, to operate the above-mentioned apparatus, first, the gas (or air) inside the vacuum vessel 1 is evacuated with a vacuum pump 2. Then the gas flow rate adjusting apparatus 5 is operated and a specified amount of gas is continuously fed to the ion-beam generator 3. The specified amount of gas mentioned here is, for example, when a vacuum pump with an evacuation capacity of approximately 100 L per second (evacuation rate) is used, the value whose upper limit is approximately 5 cm^3 per minute. Next, by operating the ion beam generator 3, the surface of the target 7 is irradiated with the ion beam of the supplied gas, the material (silicon) which constitutes the target 7 scatters in the form of atoms (atomic state) by sputtering effect, and a portion of it is adhered (deposited) on the substrate 8 which faces the target 7. And at the same time a portion of the nitrogen ions or nitrogen atom-containing ions such as ammonia ions in the ion beam of the supplied gas reach the surface of the substrate 8, therefore silicon nitride is formed and deposited on the substrate 8 as can be represented by the chemical reaction formulas, $Si + (1/2)N_2^+ + xe^- \rightarrow SiN_x$ in case of nitrogen ions, and $Si + xNH_3^+ + xe^- \rightarrow SiN_x + (3/2)H_2$ in case of ammonia ions.

The present invention is such a manufacturing method, therefore silicon nitride films can be manufactured easily even under a pressure of approximately 1×10^{-1} Pa, which makes it difficult to deposit films when conventional plasma CVD or plasma sputtering method is used because the electrical discharge cannot continue. As a result the number of collisions of the silicon atoms flying to the substrate 8 with the residual gas is reduced and the drop of kinetic energy of the silicon atoms accompanying it is suppressed. Therefore silicon atoms having kinetic energy as

high as several eV reach the substrate and the compactness of the films is accelerated. As a result films which are more compact than the silicon nitride films manufactured under the pressure of approximately 1 x 10^{-1} Pa or greater can be formed.

In the following, manufacturing examples of insulating films made of amorphous silicon nitride using the above-mentioned manufacturing methods will be explained.

(1) In the above-mentioned manufacturing method, a (10: 1 volume ratio) mixture of argon gas and nitrogen gas was used. The acceleration voltage of the ion beam at the ion beam generator 3 was 5 kV, the manufacturing pressure was 2 x 10^{-1} Pa, the temperature of the substrate was 50°C, and sputtering deposition was carried out for 200 min. As a result an amorphous silicon nitride film whose thickness was approximately 30 nm was formed (or deposited) on the substrate 8. The atomic percentage of silicon and nitrogen in the film was approximately 95% and approximately 5%, respectively. The color tone of the film was a slightly metallic gloss and its electrical resistivity was approximately 10 Ω•cm.

(2) A silicon nitride film was manufactured using the conditions used in Manufacturing Example (1) except that the mixing volume ratio of argon gas to nitrogen gas was 5: 1. An approximately 30 nm-thick amorphous silicon nitride film was formed on a substrate. The atomic percentage of silicon and nitrogen in the film was approximately 90% and approximately 10%, respectively. The color tone of the film was almost transparent, the metallic gloss visible in Manufacturing Example (1) was not seen, and the electrical resistivity was approximately 10^3 Ω•cm.

(3) A silicon nitride film was manufactured using the conditions used in Manufacturing Example (1) except that the mixing volume ratio of argon gas to nitrogen gas was 2: 1. An approximately 30 nm-thick amorphous silicon nitride film was formed on a substrate. The atomic percentage of silicon and nitrogen in the film was approximately 80% and approximately 20%, respectively. The color tone of the film was transparent and its electrical resistivity was at least 10^6 Ω•cm.

(4) A silicon nitride film was manufactured using the conditions used in Manufacturing Example (3) except that the sputtering deposition time was 20 min and a metal layer (niobium layer) was formed on the substrate in advance. An approximately 3 nm-thick silicon nitride film was formed on the metal layer. Then a further metal layer (niobium layer) was formed on the film by vapor deposition method to prepare an MIM junction (a junction made of a metal layer, an insulator layer, and a metal layer laminated in this order) having an area of approximately 1000 μm^2. The junction resistance was 10^5 Ω or greater and it was confirmed that short circuit between metal layers was not generated.

According to the above-mentioned Manufacturing Examples (1), (2), and (3), in case the atomic percentage of nitrogen in the silicon nitride film is less than approximately 10%, its

electrical resistivity is approximately the same as that of amorphous silicon film containing no nitrogen thus it is not suitable as an insulating film. Furthermore in case the atomic percentage of nitrogen in the above-mentioned film is approximately 10% or greater, the electrical resistivity is at least approximately 100-fold that of the amorphous silicon film containing no nitrogen, and even if the atomic percentage of nitrogen is less than 57%, which is the stoichiometric composition of silicon nitride (Si_3N_4), it can function as an insulating film.

And Manufacturing Example (4) shows that even in a silicon nitride film which is as thin as approximately 3 nm, a compact insulating film having no pinholes was produced which was very difficult to produce when conventional methods were used, so thus the effectiveness of the present invention is shown.

The effectiveness of the present invention is not limited to the [properties] mentioned above but is also exhibited in the manufacture of silicon nitride films of consistent high quality. This is because by controlling the pressure during the manufacture of the films to approximately 10^{-1} Pa or less, the amount of impurities in the deposited films can be reduced, therefore the fluctuation of the quality of the films can be reduced.

Application Example 2

Figure 2 shows an apparatus for manufacturing amorphous silicon nitride used in other application examples of the present invention. In Figure 2 the reference numerals 1-8 have the same meaning as reference numerals 1-8 in Figure 1. 9 is the second ion beam generator, 10 is the second gas introduction tube, 11 is the second gas flow rate adjusting apparatus, and 12 is the second gas cylinder. The gas in the first gas cylinder 6 is argon, however, it can be other inert gases such as xenon and krypton. The gas in the second gas cylinder 12 is nitrogen, however, it may be other gases containing nitrogen atoms such as ammonia gas. The target 7 is a silicon plate which has a purity of 99.999%, however, it may be a silicon nitride plate (Si_3N_4 plate). The substrate 8 is a thermally oxidized silicon wafer substrate, however, it may be other insulator substrates such as glass substrate, metal substrate, semiconductor substrate or organic polymer substrate.

Next, to operate the apparatus, first, the inside of the vacuum vessel 1 is evacuated using a vacuum pump 2. Then the first gas flow rate adjusting apparatus 5 is operated and the specified amount of gas is continuously fed to the first ion beam generator 3. The specified amount of gas mentioned here is, for example, when a vacuum pump with an evacuation capacity of approximately 100 L per second (evacuation rate) is used, the value whose upper limit is approximately 5 cm^3 per min. And the second gas flow rate adjusting apparatus 11 is operated and the specified amount of gas is continuously fed to the second ion beam generator 9. The amount of gas to be fed is the value, for example, when the evacuation rate of the vacuum pump 2

is approximately 100 L per second, that the upper limit is approximately 5 cm^3 per min. Next, by simultaneously operating the first ion beam generator 3 and the second ion beam generator 9, the surface of the target 7 is irradiated with the ion beam of argon gas, and the material (silicon) which constitutes the target is atomized (i.e., atomic silicon) by the sputtering effect, and scatters, and a portion of it is deposited on the surface of the substrate 8 which faces the target 7. At the same time, the surface of the substrate 8 is irradiated with the ion beam of nitrogen gas generated by the second ion beam generator 9, and silicon nitride is deposited on the surface of the substrate 8.

In this manufacturing method, in addition to the effect explained in Application Example 1, ionized and accelerated active nitrogen molecules can be transported to the surface of the substrate, therefore silicon nitride films containing a large amount of nitrogen can be manufactured at a pressure which is much lower than the case of Application Example 1. As a result more compact silicon nitride films with good electrical insulating properties can be obtained.

In the following, another example of manufacturing silicon nitride films using the above-mentioned methods will be shown below.

In the above-mentioned method, the ratio of the amount of argon gas fed to the amount of nitrogen gas fed was controlled to 5: 1, the manufacturing pressure was controlled to 8×10^{-3} Pa, the acceleration voltage of the ion beam in the first ion beam generator 3 was controlled to 5 kV, the acceleration voltage of the ion beam in the second ion beam generator 9 was controlled to 800 V, the temperature of the substrate was controlled to 50°C, and the operation time was controlled to 200 min, thereby an approximately 20 nm-thick amorphous silicon nitride film was formed. The atomic percentage of silicon and nitrogen in the film was 60% and 40%, respectively, thus it is clear that a silicon nitride film containing more nitrogen than the case of Application Example 1 was formed. The electrical resistivity of the film was at least 10^6 Ω•cm and good electrical insulating properties were obtained. When the amount of nitrogen in the film exceeds 40% atomic percentage, a stable silicon nitride film cannot be obtained.

As explained above, when the present invention is used, compact silicon nitride films can be deposited on the surface of substrates which were kept at low temperature, therefore, they have the advantage, for example, that they can be used as protective films for LSI and semiconductor elements which are not resistant to heat or as a diffusion mask in the manufacturing process of elements (or components).

Furthermore even when the thickness of the silicon nitride films manufactured by the present invention is several nm, they are compact films with no pinholes, therefore they are suitable as nitride films for MNOS elements or barrier films of tunnel-type Josephson elements.

Brief description of the figures

Figures 1 and 2 show a silicon nitride manufacturing apparatus, respectively, used in carrying out the present invention.

In the figures, 1...vacuum vessel

2...vacuum pump

3 and 9...ion beam generator

4 and 10...gas introduction tube

5 and 11...gas flow rate adjusting apparatus

6 and 12...gas cylinder

7...target

8...substrate.

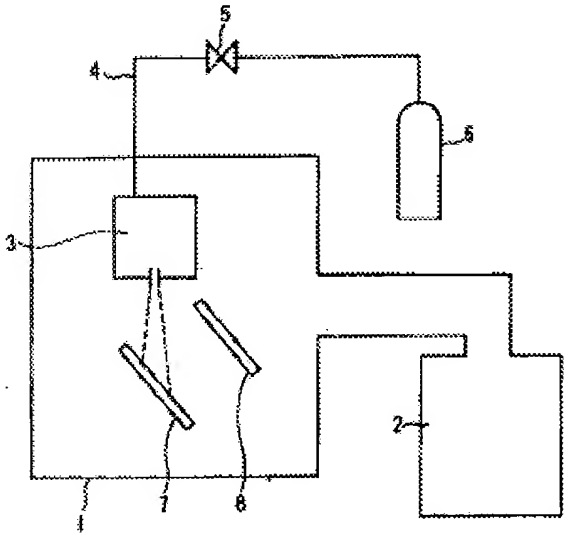

Figure 1

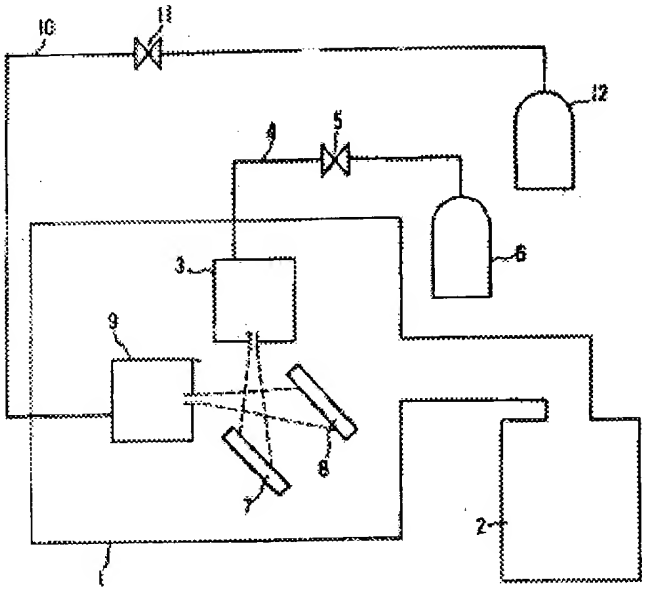

Figure 2